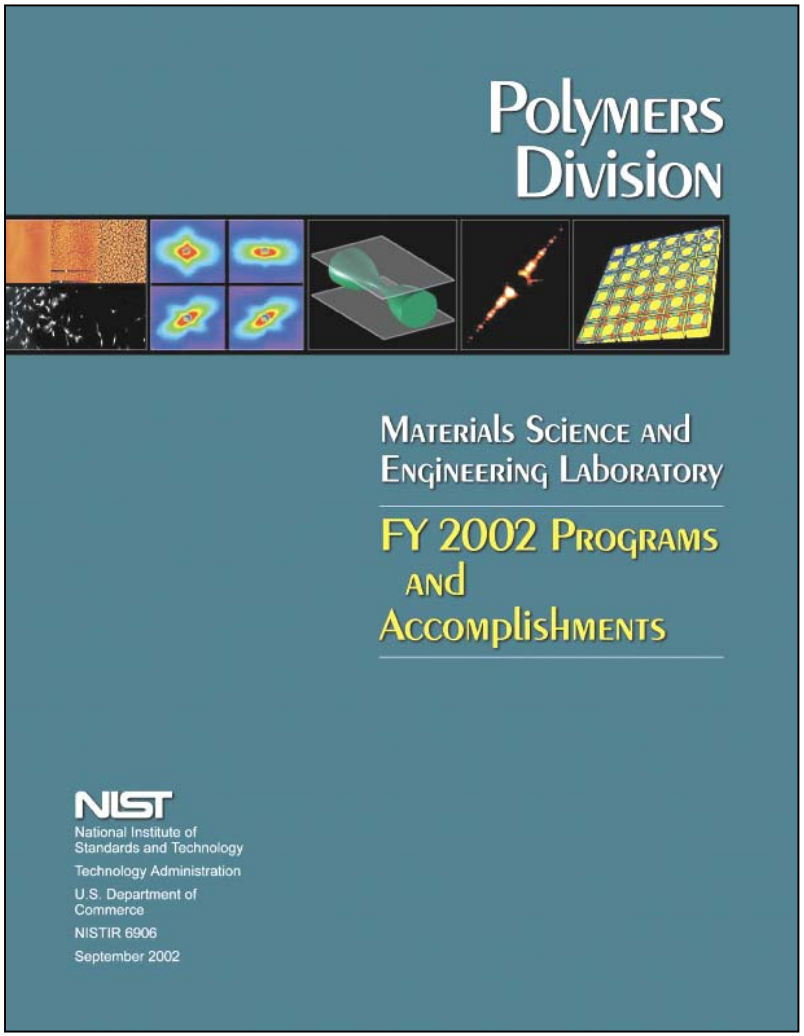
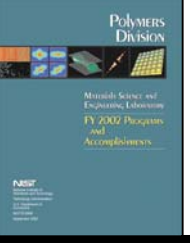
Polymers

Materials Science and Engineering



Polymers Division: Multivariant Measurement Methods

- Overview
- NCMC / Informatics
- Formulations / Fluidics
- Adhesion & Mech. Prop.
- Future Directions

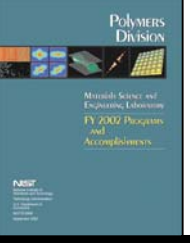


Project Objectives

- Adhesion: Develop multivariable methodologies to probe the adhesive strength at polymeric interfaces. To continue establishing our expertise in combinatorial adhesion tests.
- Modulus: To pursue our measurement method (SIEBIMM) for determining the mechanical properties of polymer thin films, with emphasis initially on scientific discovery as well as customer application.

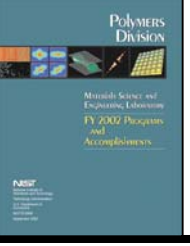
- Held NCMC Workshop on Combinatorial Adhesion & Mechanical Properties (October 2002).
  - Dissemination
  - Information gathering / strategic direction

- Major Customers:
  - Adhesion: 3M, Rohm & Haas, Air Products
  - SIEBIMM: IBM, Dow, academics



Project Overviews

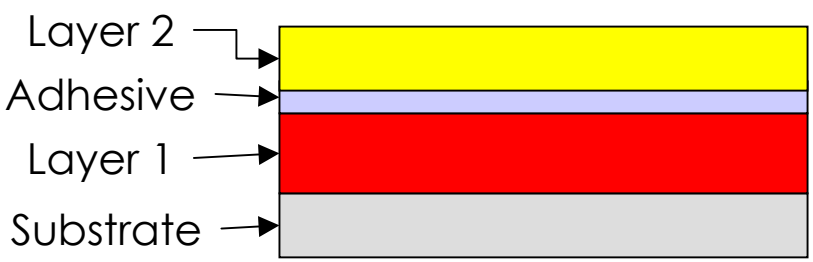
- Publications & Patents:
  - Patent application, Invention: Method for Combinatorially Measuring Adhesion Strength, submitted 6/02.
  - A.J. Crosby, A. Karim, E.J. Amis, "Combinatorial Investigations of Interfacial Failure", *J. Polym. Sci. B: Polym. Phys.*, accepted.
  - Song R., et al. “Combinatorial approaches to thin film adhesion as a function of film thickness and surface energy," *in prep*.
  - Song R., et al. “Combinatorial measurements on the adhesion of PMMA ultrathin films," *in prep*.
  - Harrison, C., Stafford, C.M., Beers, K.L., Amis, E., Karim, A.; “Strain Induced Elastomer Buckling Instability for Mechanical Measurements”, *in prep*.



Adhesion Overview

- Adhesion is a complex phenomenon – critical area of material science.
- Adhesives are some of the most highly engineered materials – yet some of the least understood.
- Knowledge generation is pivotal to future success of adhesives.

- Adhesive
  - chemistry
  - architecture
  - additives
  - tackifiers
  - processing
- Substrate
  - composition
  - surface energy
  - roughness
  - chemistry
- Forces
  - van der Waals
  - entanglements
  - covalent bonds
  - viscoelasticity (dissipative)

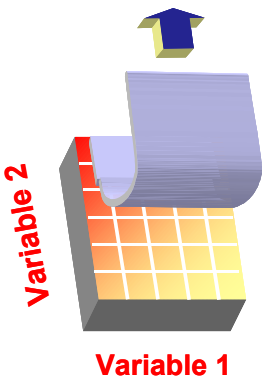


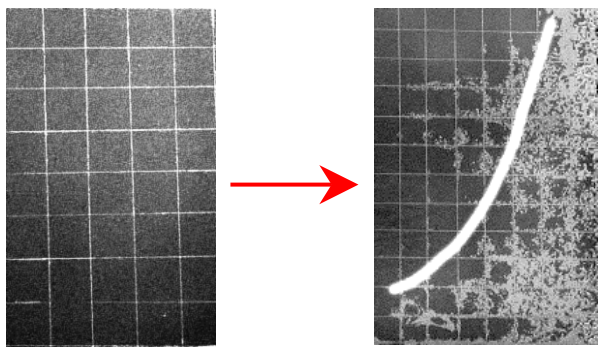
Combinatorial Peel Tests

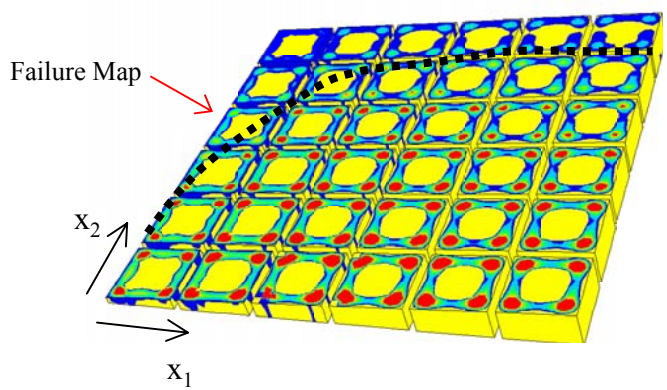
- Industrial Standard – 180^{o} Peel Test (ASTM D903-98)
- Single sample with given set of processing parameters
- Introduce combinatorial sample design and apply to peel test
- Experiments were in parallel with finite element analysis simulations.

- casting solvent **- annealing history** **- surface chemistry**

Song R., et al. "Combinatorial approaches to thin film adhesion as a function of film thickness and surface energy," *in prep*.
Song R., et al. "Combinatorial measurements on the adhesion of PMMA ultrathin films," *in prep*.

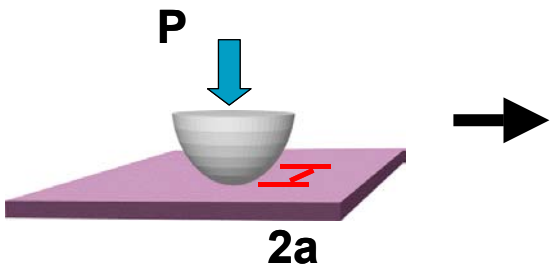


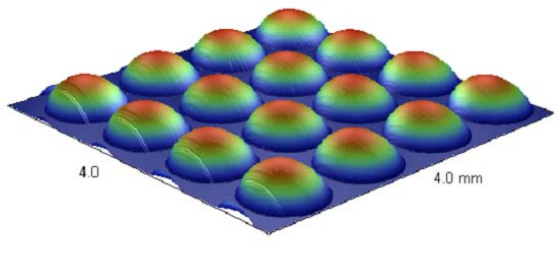




Combinatorial JKR Adhesion Tests

- Traditional
  - Single lens
  - Load, contact area measured
  - Work of adhesion, modulus determined
- Multiple microlenses
  - Array of 1600 lenses covering 1 cm^2
  - The resolution provided with this array is smaller than required by the typical sample gradient.
- Multiple microlenses
  - Array of 324 larger lenses covering 3.25 cm^2
  - The lens size is better suited to the typical sample gradient.

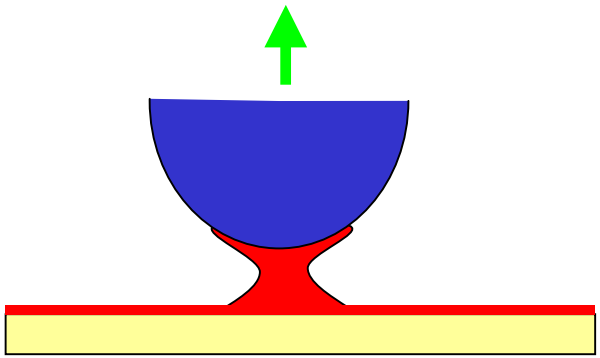


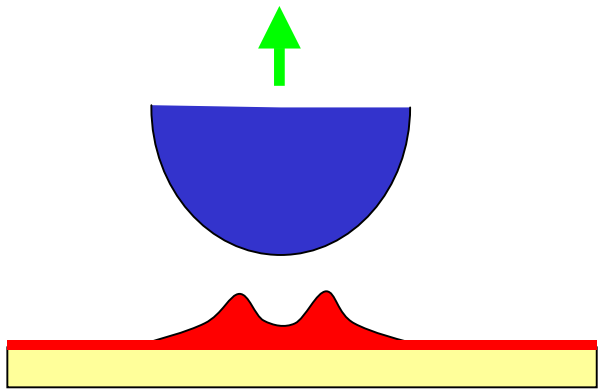


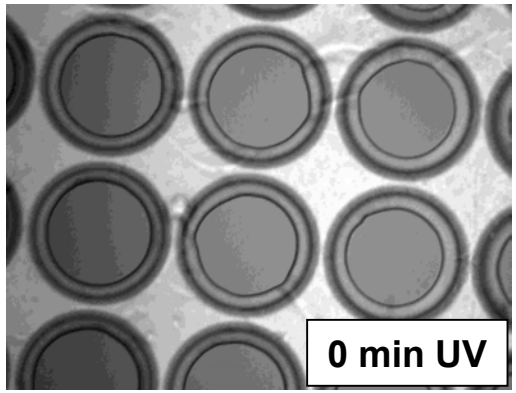
$$G = \frac{3(P'-P)^2}{32\pi E a^3}$$

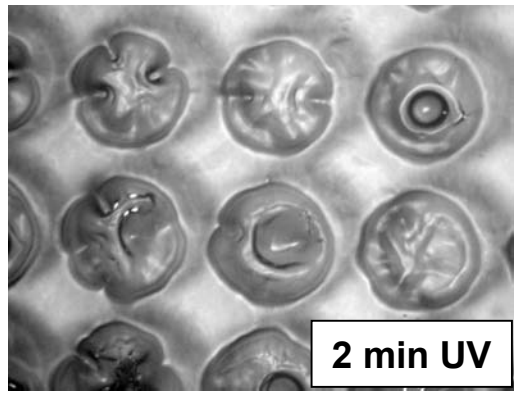
$$G = \frac{2E(\delta' - \delta)^2}{3\pi a}$$

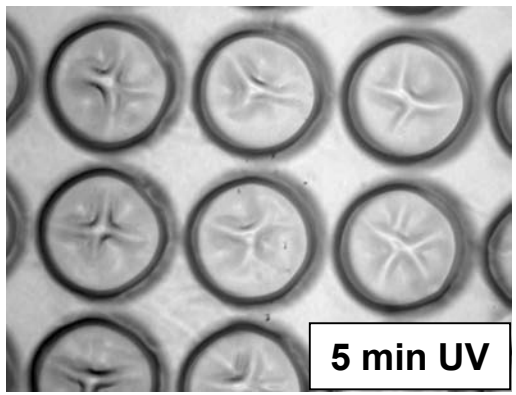
Pressure Sensitive Adhesives

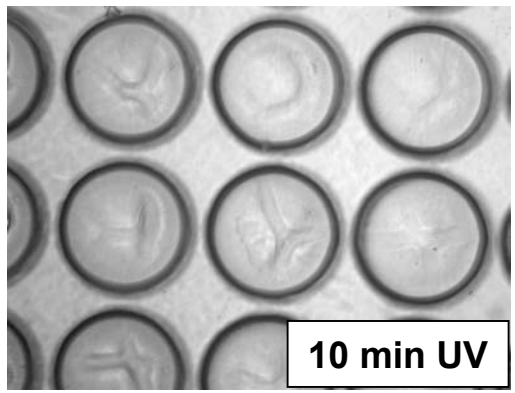








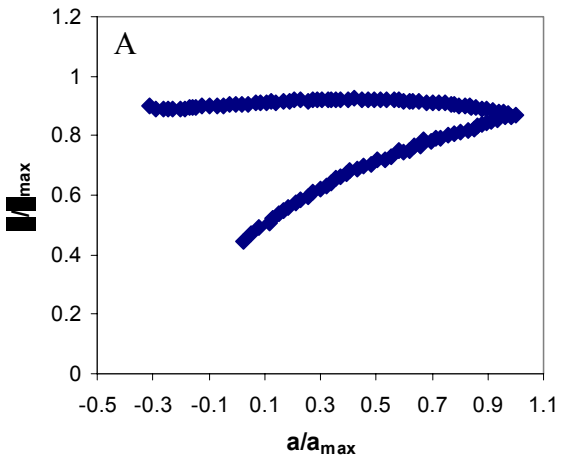


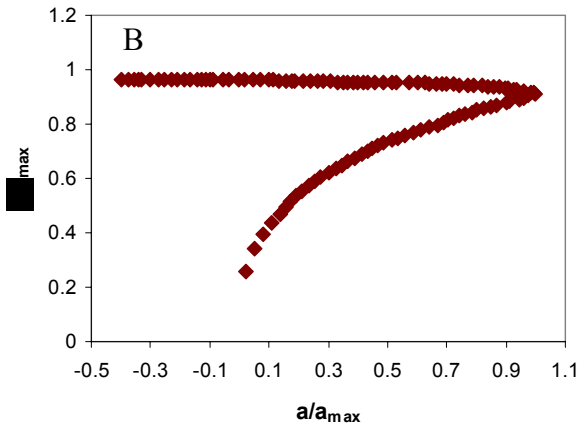


Irreversible Viscoelastic Deformation

Epoxy Curing on Temperature Gradient

The initiation temperature to cure the epoxy resin is evident through hysteresis in the loading and unloading cycles.



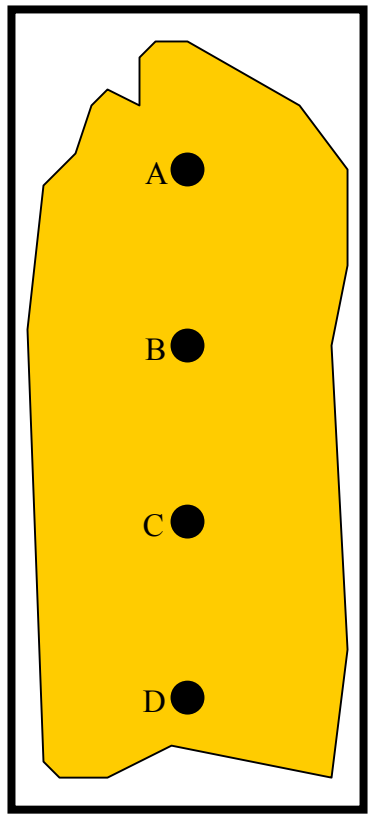


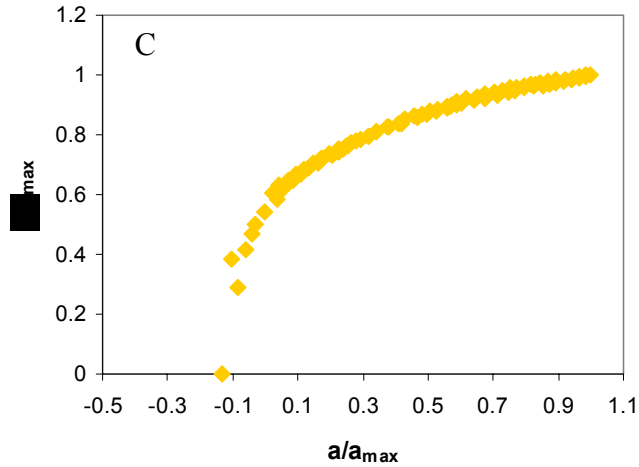
Curing Temperature

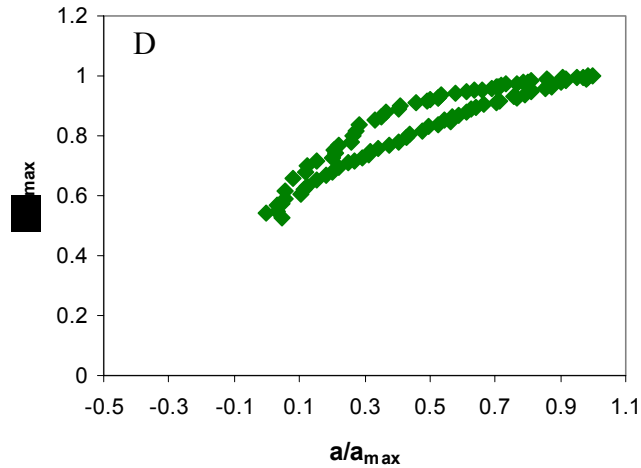
50 °C

70 °C

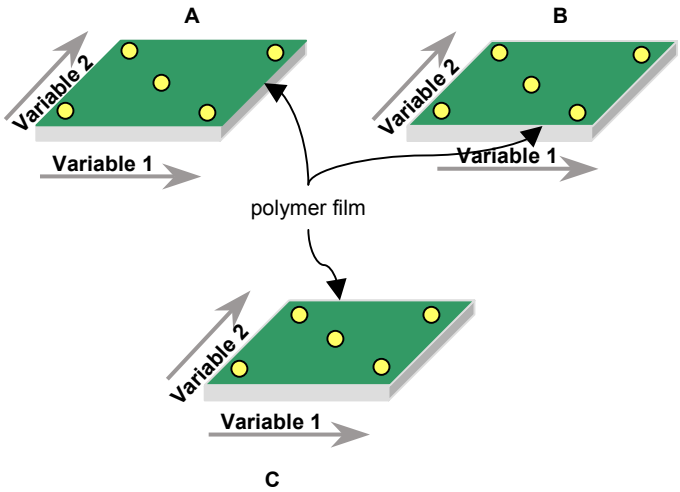
86 °C



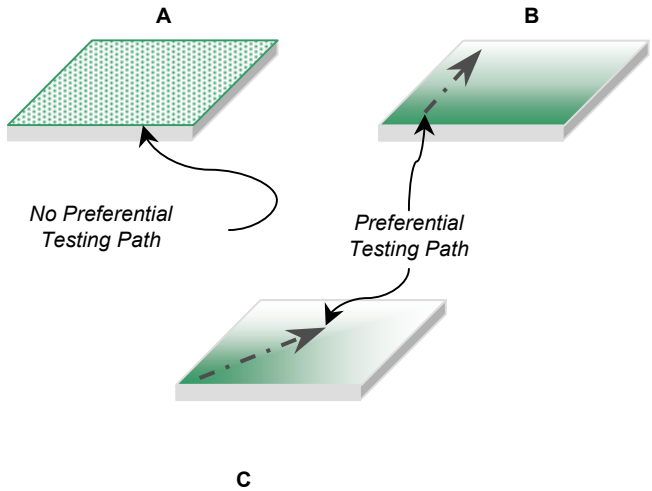




Design of Experiments

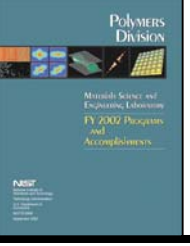


Adhesion is measured across the sample in a few areas (yellow spots).



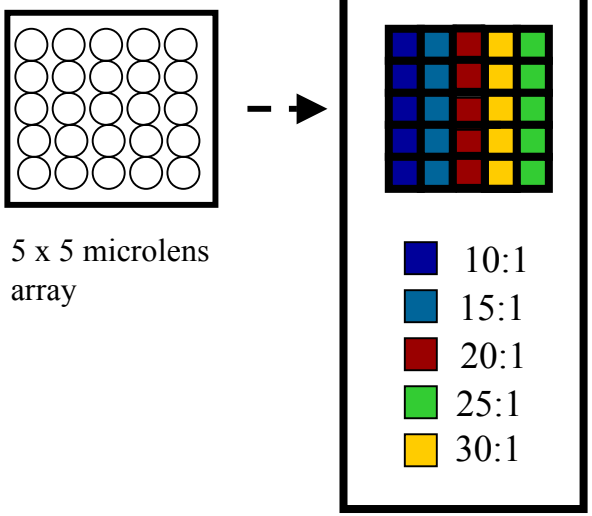
A representative surface map is created by following the *Preferential Testing Path.*

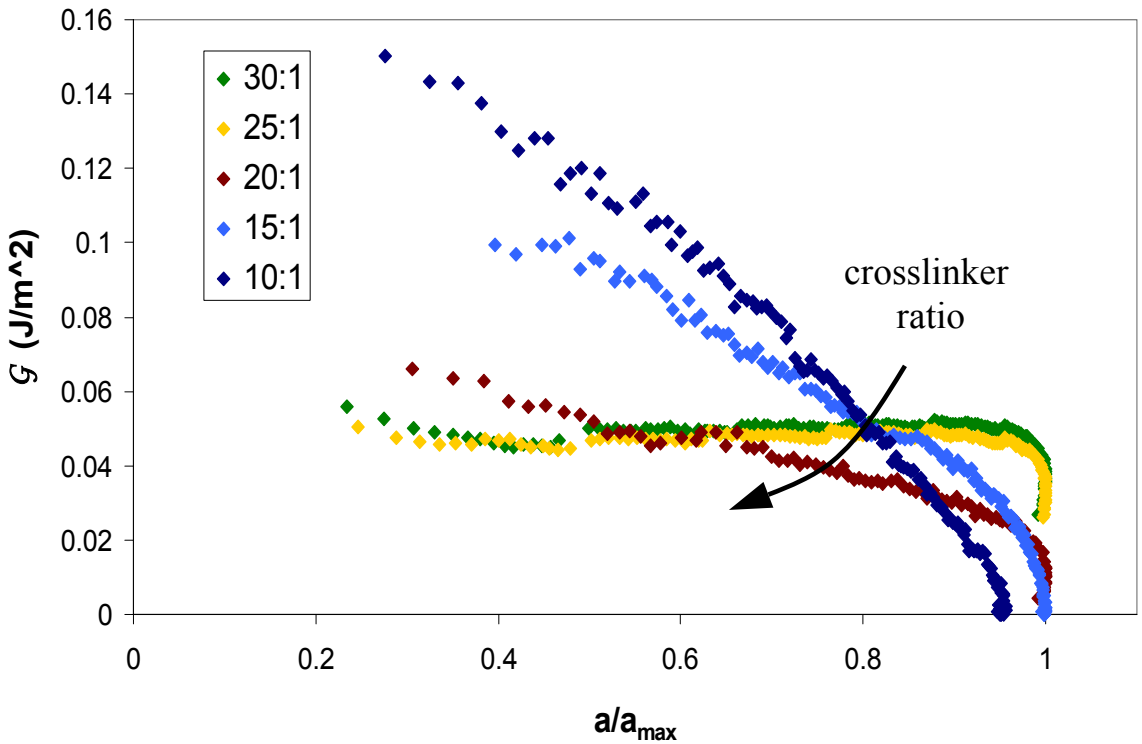
- A mismatch exists between the size of the lens array and the gradient library.
- Potential data overload exists if the whole gradient library is evaluated.
- The design of experiments approach reduces the number of experiments through statistical evaluation of the gradient library to determine the most efficient testing path.



DEX with PDMS

- An array of wells are created utilizing bench-top lithography.
- These wells serve as casting basins for creating discrete samples for adhesion analysis of a non-continuous gradient.
- Paves the way for multidimensional (>2) parameter space which is pivotal for industrial adhesives and formulations.

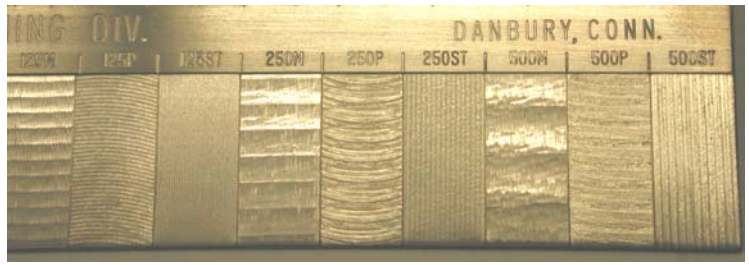




Adhesion to Rough Surfaces

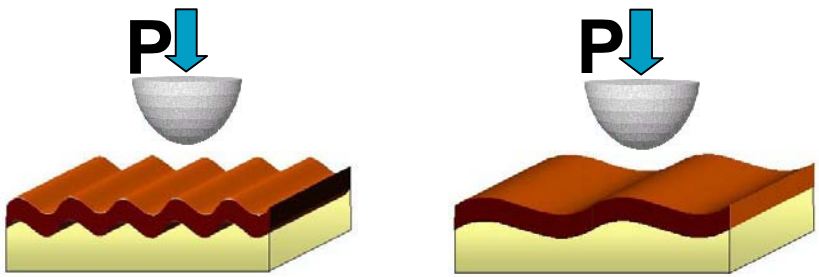
- All surfaces are rough
- The scale of surface roughness can either promote or prevent adhesion.
- NIST is interested in quantifying the influence of model rough surfaces or roughness standards on adhesion.

machined/milled



Processed surfaces are more industrially relevant surfaces.

Sinusoidal surfaces are great for comparing to theoretical models.

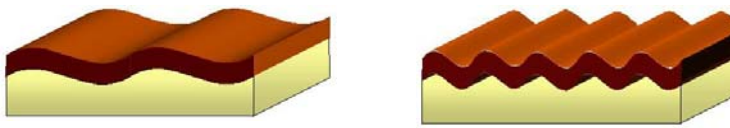


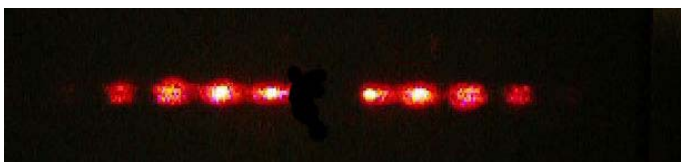
shot-blasted

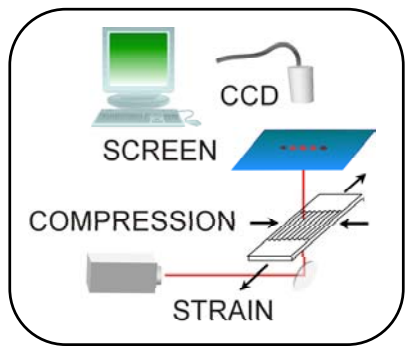
HT Modulus of Polymer Films

- There is a growing need for test methods that can measure the mechanical properties (modulus, viscoelasticity, plastic deformation) of thin films.
- We have developed a simple, high-throughput technique that exploits a buckling instability that results from compression of a laminate.
- Wavelength can be related to material properties such as modulus.

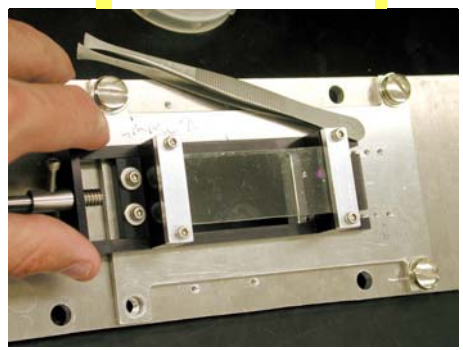
$$d \sim h\left(\frac{E_p}{E_m}\right)^{1/3}$$



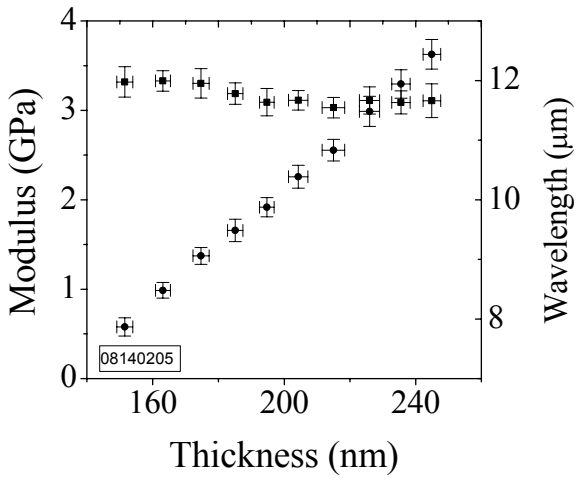


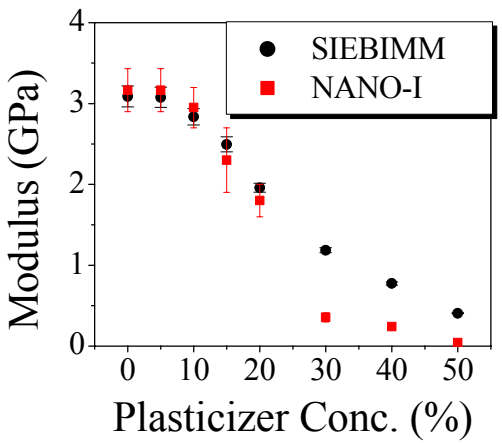


No Strain



HT Modulus of Polymer Films





NIST: DIRECTOR ARDEN BEMENT STRIVES FOR GLOBAL REACH

CHEMICAL & Engineering News

COVER STORY

vative screens. "It's a good outfit to be hooked up with," says Menas S. Vratsanos, who leads a polymer characterization group at Air Products. "I think we're getting more than our money's worth."

Dow Chemical, which has an extensive in-house R&D effort in combinatorial methods and has participated in several NIST consortiums, also sees value in being part of the new combi center. NCMC's approach to synthesizing and screening combinatorial libraries is unique, remarks chemist Don Patrick of Dow. "We wanted to learn more about the applicability of these approaches to our materials programs." Participating in the center "also allows us to network with other companies that have an interest" in polymer characterization, Patrick says.

Some NCMC members would like to have a hand in directing or influencing future efforts at the center. Procter & Gamble, for instance, is particularly interested in high-throughput methods for measuring interfacial tension, according to P&G chemist Pramod K. Reddy. "Interfacial tension is an extremely important parameter that we measure day in and day out" in the company's fabric and home care division, he explains. It's of interest for almost all cleaning products, including laundry detergents, dish detergents, and shampoos, because it can be indicative of their cleaning ability.

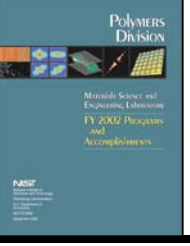
Using existing methods, industry scientists may be able to make 10 to 20 measurements of interfacial tension per day, according to Reddy. They would like to have the capability of making hundreds of such measurements per day, but the requisite high-speed measurement tool does not exist—yet. P&G is hoping that if other NCMC members agree that such a tool is a priority for them, too, the center will take up the challenge. Reddy is confident that NCMC "should be able to develop the tool fairly quickly—I would say less than two years' time." A third part would then be approached to manufactur the instrument, whic could be purchased by company and applied t product development.

Even if NCMC doe not develop exactly wha some member companie need for their particula problems, Amis explain his hope is that compan scientists will start think ing differently about th way they're approachin their problem, and mayb they'll be able to use th new way of thinking t develop something that exactly what they want.

"Quite often," Ami says, "people will look what we're trying to do an they'll tell me, 'Oh, yo can't measure that wit combi.' Now that's th sort of challenge I love."

IN A FLASH Postdocs Christopher K. Harrison (right) and Christopher M. Stafford with the light-scattering system they developed to measure the elastic modulus of thin-film polymer libraries in a high-throughput manner.

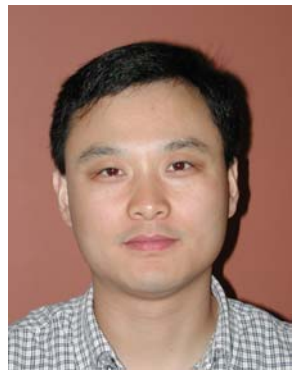
- Currently working with IBM and Dow on characterizing porous low-k materials.
- Also exploring clay nanocomposites and branched polymers.



Project Members

Team SIEBIMM:


Team CAD:




Team MCAT: